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Part I. Thermal Decomposition Products of Cellulose

Cellulose powder was decomposed thermally under atmospheric pressure at 350°C. Furfural and acetaldehyde have been isolated from the products as their 2,4-dinitrophenylhydrazones and the following compounds have been identified by paper- and gas chromatography: formic, acetic, propionic, iso- and n-butyric acids, propionaldehyde, butylaldehyde, phenol and o(m)-cresol. The amounts of furfural and acids (formic and acetic) were 1.4% and 1.1% of cellulose, respectively. The water content was about 79% of products and it corresponds to 30% of cellulose dry matter. The weight loss of cellulose when heated at continuously rising temperature in air was remarkable at a

temperature range of 250-350°C. Both formation of furfural and destruction of cellulose were also extremely high under the conditions applied herein. From the results of quantitative determination of furfural among the decomposition products of cellulose and levoglucosan, it was suggested that cellulose was not always decomposed through levoglucosan.

(Received June 14, 1966)

Preface

Chemical composition of a cigarette smoke includes substances generated by the thermal decompositon and substances which are transported into smoke without chemical change in the form they existed in a tobacco leaf. Cellulose represents 10% of a tobacco leaf (as coarse fibre)[1] and it is the main ingredient of a cigarette. Analyzing the pyrolysis of cellulose, the authors attempted to clarify its effect on fragrance in cigarette smoking.

The heat resistance of cellulose varies with external factors such as temperature, time duration and gas atmosphere at heating and with internal factors such as polymerisation and purity of the test material.[2] In this experiment, cellulose powder was thermally decomposed in air, carbonyl

compound produced is lead to 2,4 - dinitrophenylhydrazones (2,4 - DNP), furfural and acetaldehyde are isolated as derivatives, then by either paper chromatography (PPC) or gas chromatography, butyloldehyde, propinaldehyde, formic acid, acetic acid, propionic acid, phenol and O(m) - cresol are identified. Also the amount of water generated by the pyrolysis of cellulose reached 30% of cellulose.

As it is reported in the previous report,[3] furfural is also generated by the thermal decomposition of glucose which is a unit constituent of cellulose, therefore the quantity of furfural produced during cellulose heating is investigated with levoglucosan which is known to be an intermediate state of cellulose pynolysis.

Experiment

1. Test Material

For the experiment, cellulose powder (produced by Toyo Filter Paper for chromatography usage, 100-200 mesh) is used. The material contains 6.94% water and 0.08% ash.

2. Thermal Analysis

300mg of cellulose powder is collected in platinum crucible. Using To-ko-shi style thermal balance the temperature gradient in air is controlled to 2 degrees per minute. By heating, powder volume is reduced. As illustrated in the Figure 1, continuous heating versus volume reduction curve is obtained.

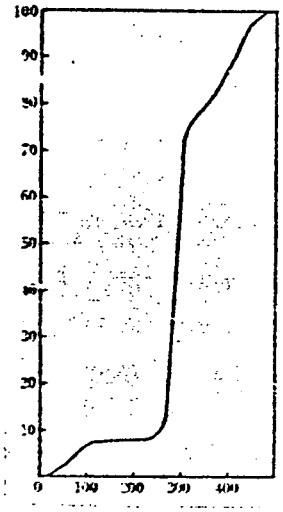


Figure 4. Curve of Cellulose Volume Reduction by Heating

Test Material: Cellulose Powder 300 mg

Temperature Rising Rate: 2 °/min in Air

Equipment: To-ko-shi Style Thermal Scale

3. Method of Pyrolysis

Pyrolysis of 20 mg cellulose in heat resisting glass flask is performed in a vertical electronic furnace. The furnace temperature is measured by the aluminum-chromium thermocouple thermometer. The heat is increased to 350° with 10°/min to 15°/min rate then at 350° the furnace is heated for an hour. At the furnace temperature 250°, light-yellow oily substance flows out. As the temperature rises, the color of the discharge fluid darkens. At above 300°, it becomes dark brown. After 30 minutes of heating at 350°, a flow of the decomposed product almost ceases. Repeating the operation five times, 45.4 grams of the discharged materials and 39.1 grams of the decomposition remnant are obtained from 100 grams of cellulose.

4. Extraction and Classification of Pyrolysis Derivatives

Decomposition derivatives were trapped by connecting 200 ml bottle containing 100 ml of 0.4 % 2,4-DNP hydrochloric acid solution to a coolant cooled trap. 45.4 grams of the trapped decomposed product is removed by five extractions with 50 ml of ether and one extraction with salt saturation.

The ether solution is classified as illustrated in the Figure 2. 2.05 grams of acid portion, 0.45 grams of phenol portion, 0.44 grams of neutral portion and carbonyl portion are extracted. To the carbonyl portion, an ample quantity of 0.4% 2,4-DNP hydrochloric acid solution is added. Filtering out sedimentation, 5.7 grams of reddish brown 2,4-DNP derivatives is obtained. To the filtered solution, again 2,4-DNP hydrochloric acid solution is added. After letting them settle overnight, 0.4 grams of orange colored 2,4-DNP derivative is extracted.

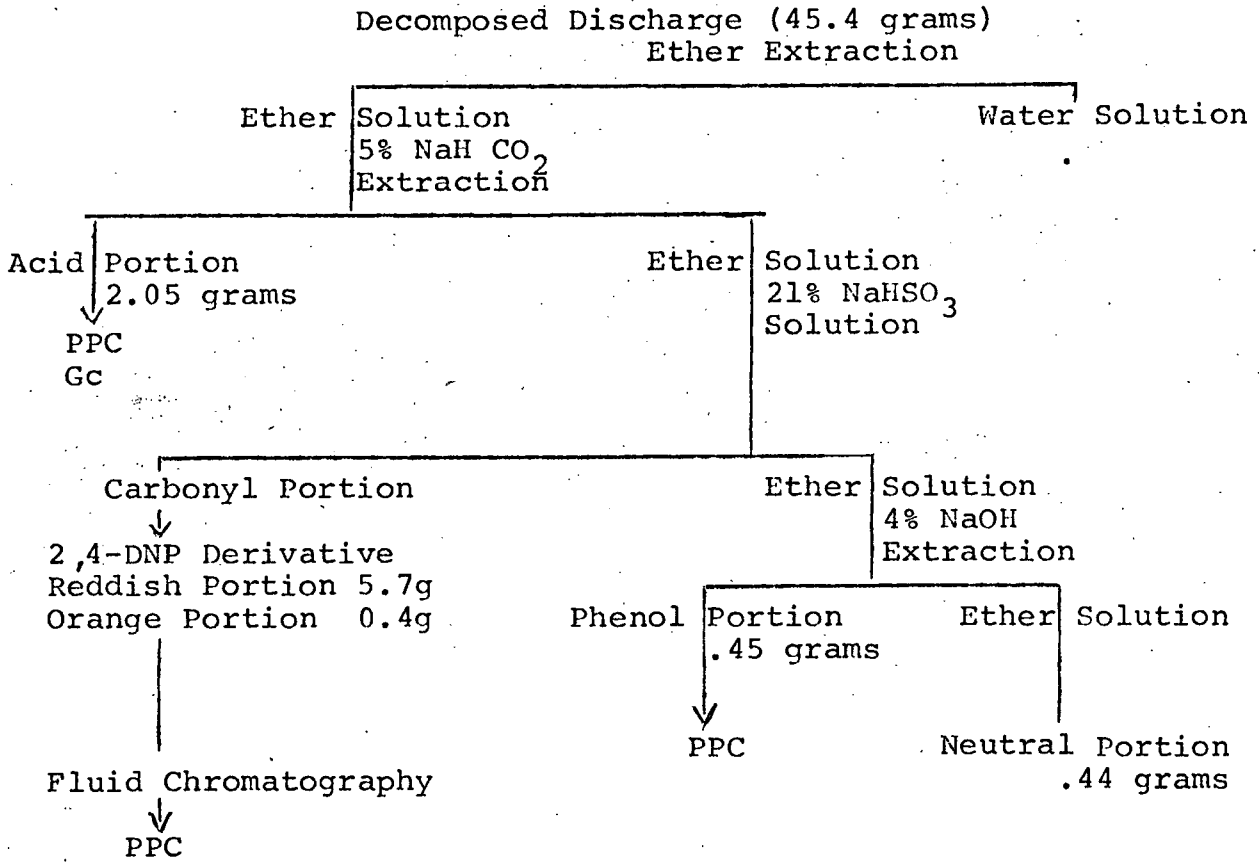


Figure 2: Classification of Pyrolysis Derivatives

5. Water Content of Decomposition Product

50.0 grams of the test material is heated at 350° for an hour. The decomposition product is dissolved in 5 to 1 pyridine-ethlene glycol mixture. Taking 20 ml of this solution, the water content is measured with Carl Fisher water content measurement apparatus. The water content of the decomposition product is 78.6%. This is 30% of cellulose dry matter.

6. Paper Chromatography of Acid Portion

The acid portion of Figure 2 is applied as a spot on Toyo Filter Paper No. 51. The mixture butanol water diethylamine (100:15:1)[6] is employed as the developing solution. The spot is permitted to develop for 15 hours by rising room temperature method. Then 0.05% citric acid BCG is sprayed to color. Comparing with samples, acetic acid (R_f 0.32), propionic acid (R_f 0.39), and n-butyric acid (R_f 0.51) are identified.

7. Analysis of Inorganic Acid by Gas Chromatography

Inorganic acid in the thermal decomposition products is analyzed by gas chromatography. This is the same method employed by Yoichi Kabuki and Yuriko Sato to analyze volatile acid in a tobacco leaf.[7] As the previous experiment, 20.0 grams of cellulose is heated for an hour at 350°. The acid portion of decomposition products is methylized by diethylmethane to produce methyl esters. Using gas chromatograph (Model GU-12, produced by Kotaki Mfg. Co.), methyl ester is

analyzed with acetic acid as a standard. The test condition was PEG 1,500; column length 2.5 meter, temperature 57° and helium velocity of 40 ml/min. Using the gas chromatogram in Figure 3, retaining period is compared with methyl ester in inorganic sample. Then formic acid and iso-butyric acid are isolated in addition to the acids identified by PPC. Table 1 illustrates the corrected assay values after consideration of collection ratio. The quantity of formic acid and butyric acid in the acid portion is quite large. The combined quantity is equivalent to 1.1% of cellulose.

Table 1 Quantities of Acids Produced by Thermal Decomposition of Cellulose*

Inorganic Acids	Quantities (mg)	Recovering Ratio**(%)
Formic Acid	98.5	32.1
Acetic Acid	112.9	47.7
Propionic Acid	48.4	79.0
Iso-butyric Acid	13.6	95.6
n-butyric Acid	3.1	----

*Cellulose powder 20g, 350°, 1 hour heating.

**Average recovering ratio, based on 3 samples.

Table 2 Liquid Chromatogram of 2.4 - Dimtrophenylhydrazones of Carbonyl Portion

Band Number	Color on Adsorbent Column	Developing Solution Composition Benzene: Ligroin	Product Quantity (gram)
1	Yellow	40:60	.006
2	Yellow	40:60	.284
3	Orange	50:50	.112
4	Red	50:50	.273

Remainder Reddish Brown

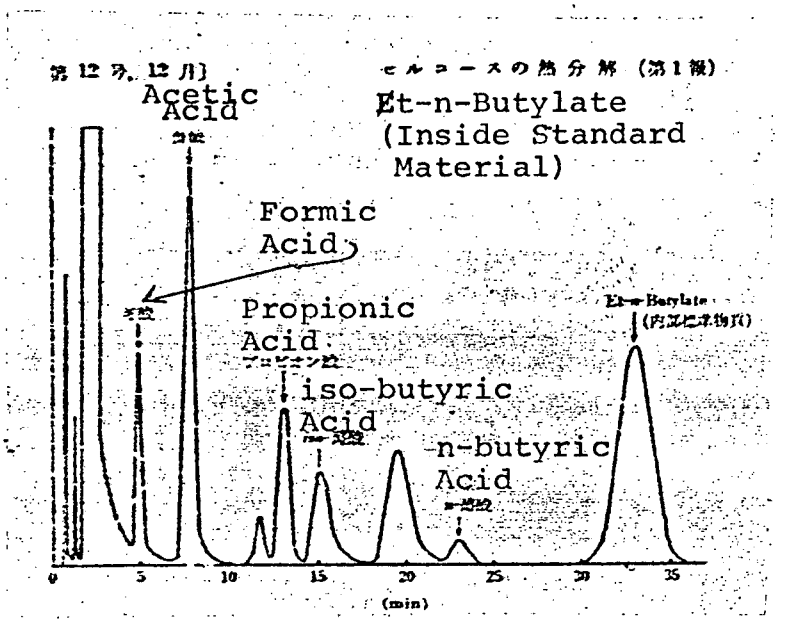


Figure 3

Gas Chromatogram by Methy Ester for Acids Produced by Thermal Decomposition

Column: PEG 1,500. 2.5m Temperature: 57° Carrier Gas: He 40ml/min

8. Separation and Identification of Furfural 2,4-DNP

5.7 grams of 2,4-DNP derivatives of carbonyl portion in Figure 2 is dissolved in 30 ml of chloroform. Undissolved portion is filtered out and placed at the top of alumina column of size 3x20cm. Then according to the method of Takahiro Ueno and Akio Nobuhara,[8] the substance is developed by benzene-ligroin mixture. The result is illustrated in Table 2. 100 ml of solvent in band 2 is condensed by pressure reduction and 0.28 grams of yellow crystals are obtained. The recrystallization of these crystals is repeated in ethanol. The refined crystals have the melting point between 200° and 202°. Its infra red absorption spectral matches furfural 2,4-DNP of type cis sample. The crystals do not lower the melting point in mixed examination.

Elementary Analysis.

Computed value, based on $C_{11}H_8N_4O_5$: C 47.83, H 2.89, H 20.29%

The experiment value: C 48.13, H 3.03, N 19.92%

From these results, the crystals are identified as furfural 2,4-DNP of type cis.

100 ml of solvent in band 4 is condensed and 0.273 grams of red crystals are obtained. Then the substance is refined by flowing through alumina column of a size 1x15cm using benzene-ligroin (50:50) mixture as developing solution. The refined crystals have the melting point at 227° and match infra red absorption spectral of furfural

2,4-DNP of type trans sample. The crystals do not lower the melting point in mixed examination therefore this is identified as furfural 2,4-DNP of type trans.

9. Separation and Identification of Acetaldehyde 2,4-DNP

0.4 grams of orange colored 2,4-DNP derivatives of carbonyl portion in Figure 2 is dissolved in 30 ml of chloroform. After filtering out undissolved portion and gradually separting the solvent, 10 ml of the solution is obtained. Then this is developed by flowing through the alumina column of a size 2x13 cm using benzene-ligroin (40-60) mixture as developing solution. 200 ml to 400 ml of the resulting solution is condensed and 0.18 grams of crystals are obtained. These crystals are recrystallized in ethanol. The refined yellow needle like crystals have the melting point of 163°. Its infra red absorption spectral matches the acetaldehyde 2,4-DNP sample and the melting point is not lowered in the mixed examination.

Elementary analysis:

Computed values based on - $C_8H_8N_4O_4$: C 42.86, H 3.60, N 24.99%

The experiment values: C 42.97, H 3.50, N 24.47%

From these results, the crystals are identified as acetaldehyde 2,4-DNP.

10. Paper Chromatography of 2,4-DNP

2,4-DNP derivatives which is produced by thermal decomposition and trapped in a gas trapping bottle, is

extracted in chloroform. After dehydration by sodium sulfate decohydrate, chloroform is separated and 0.18 grams of reddish brown paste like substance is obtained. The substance is refined by flowing through alumina column of a size 1x16 cm using benzine-ligroin (50-50) mixture as developing solution. The resulting solution is condensed. Then according to the method of Tetsuo Hino and others,[9] the filter paper (Whatman No. 1) is soaked in 0.1% solution of N-N' dimethylform amidoether, ether is then evaporated at room temperature and the test substance is spotted on the filter paper. Development is performed by room temperature ascending method with N-N' dimethylform amido-saturated decaline solution. Comparing with 2,4-DNP sample of carbonyl compounds, spots corresponding to acetaldehyde (R_f 0.50), propionaldehyde (R_f 0.63), n-butylaldehyde (R_f 0.75) and furfural (R_f 0.30) derivatives are identified.

11. Paper Chromatography of Phenol Portion

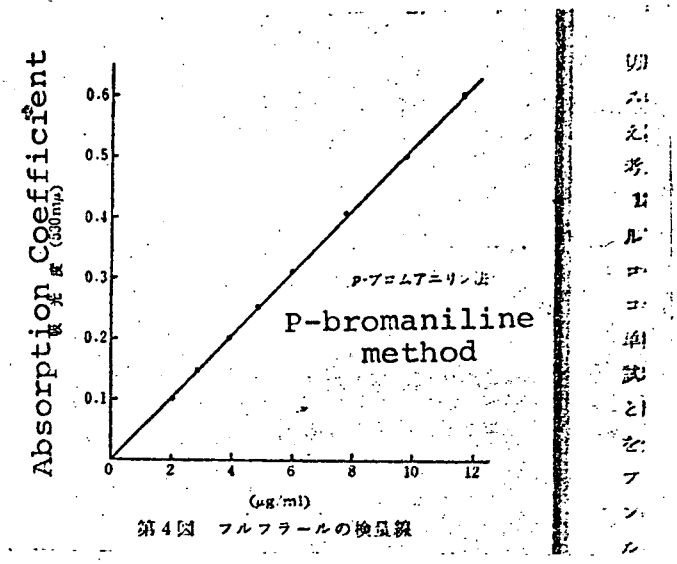
Phenol portion is lead to phenol-iso-benzene-sulfonic acid pigment derivatives. According to the method of Wen-Hua Chang and others,[10] the test material is spotted on Toyo Filter Paper No. 51 which has been sprayed with sodium carbonate and developed by room temperature descending method with sec-butanol 2% sodium carbonate as its developing solution. R_f values and colors are compared with samples of pigment derivatives of phenol type. Corresponding spots to phenol (R_f 0.31, yellow) and O(m)-cresol

(R_f 0.53, yellow) are identified.

12. Change in Cellulose Chemical Composition by Heat Addition and Temperature Effect on Furfural Production

From 200° to 400°, at every 50°, 10 grams of furfural is heated for 30 minutes. As heating temperature increases and the decomposition process proceeds, the color of the test materials changed from white at 200° to brown, dark brown and finally to black. The decomposition discharge and the heating remnant are extracted by xylene. After dehydration by sodium sulfate decahydrade, 200 ml of the materials are measured. Furfural in the xylene solution is compared for color and measured by p-bromaniline method.[11] As soon as 1 ml of furfural-xylene solution is added to 5 ml of p-bromaniline test chemical (2 grams of p-bromaniline is dissolved into 95 ml of thiourea saturated ice acetic acid and 5 ml of distilled water) the mixture is shaken and left to stand in a dark room for 30 minutes at room temperature. Then using FPW-4 photoelectric photometer (produced by Hitachi), the absorption coefficient is measured at 530 mμ and from furfural quantity determination curve in Figure 4 its quantity is determined. The heating remnant is extracted by xylene, washed by ether, etanol, hot water and acetone, and dried by pressure reduction method. 1 gram of the dry test material is hydrolysised by 72% sulfuric acid method,[12] and the undissolved portion is filtered. Then the reduction capability is measured by Somogy method.[18] The

calculation shows that the undissolved portion is glucose.



第4図 フルフラールの検量線

Figure 4 - Furfural Quantity Determination Curve

The result of furfural production by heating and the acidic hydrolysis of heating remnant are illustrated in Figure 5. Furfural production rapidly increases by heat addition at between 250° and 350° and at 350° it reaches 1.4% of cellulose. On the other hand glucose unit in the heating remnant decreases rapidly by heat addition at between 250° and 350°. From this experiment, it can be considered that when heated at between 250° and 350°, cellulose dehydrates as it decomposes also as a reaction of contraction, the severance of glucose B-1,4 bond or the change in the chemical composition of cellulose brings a composition change in pyranoside and it changes to the composition without acid hydrolysis, for an example, to the aromatic composition of the kind Sugiro Otani and others mention.[14]

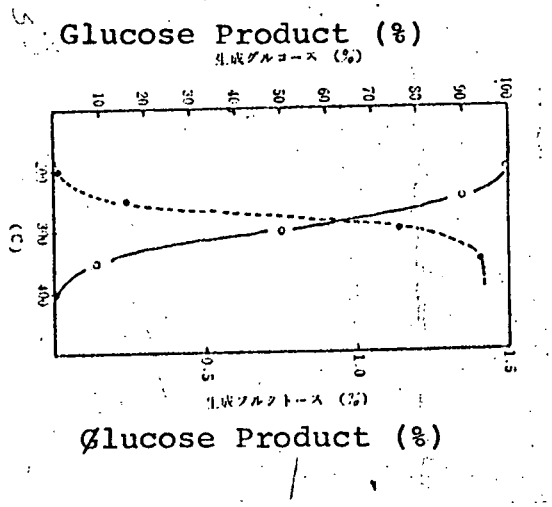


Figure 5 - Effect of Heating Temperature to Furfural Production and Change in Chemical Composition of Cellulose

13. Quantity of Furfural Products by Heating of Levoglucosan and Glucose

According to the mechanism of cellulose decomposition by Levoglucosan hypothesis,[4] cellulose → levoglucosan → furfural lineage is compared and studied with glucose which is the monosaccaride constituent of cellulose. 100 grams of each test material in 10 ml capacity flask is heated for an hour at 350° and quantities of furfural product are analyzed. When the afore-mentioned decomposition lineage is considered, it is anticipated that levoglucosan decomposition produce more furfural than cellulose decomposition. However quantities of furfural product from cellulose, levoglucosan and glucose pyrolysis decreases in this order and they are 13.5 mg, 10.4 mg and 8.7 mg respectively.

Observation

Recently C. T. Greenwood et al.,[15] R. F. Schwenker et al.,[16] S. Glasser et al.,[17] connecting the thermal decomposition apparatus directly to gas chromatography,

analyzed cellulose decomposition products and confirmed the following derivatives: Formaldehyde, acetaldehyde, propionaldehyde, glyoxol, acrolein, acetone, 2-methylfuran furfural, 5-hydroxymethyl furfural, methylethyl ketone and acetic acid. Besides these decomposition products already formic acid, glucollic acid, lactic acid, maltol, 8-voleroolactone, furan derivatives, phenol family, and benzene are reported.[2, 18] In this experiment, productions of butylaldehyde, propionic acid, iso-butyric acid and n-butyric acid are confirmed.

In 1955 R. Esteve et al.[4] advocated the levoglucosan theory about the mechanism of cellulose thermal decomposition. Also some reparts [16-18] are written to support this theory from the analysis of decomposition products. However many of cellulose decomposition products are very similar to decomposition products of glucose which is the constitutent monosaccaride of cellulose. Also the results of comparison and analysis of furfural decomposition products indicate that cellulose decomposition produces more furfural products levoglucosan decomposition. The decomposition lineage of cellulose - levoglucose - furfuran is not positively satisfied. Although it is not completely clear about the mechanism of furfural product from cellulose and hexose, there are two theories. The one theory is the secondary decomposition of 5-hydroxymethyl furfural.[8] Also E. J. Murphy[20] reported that when cellulose is heated at 160^{o} in vacuum, H_2O, CO_2 and CO are produced. It is con-

ceivable that carbon atoms free themselves from cellulose and produce pentose unit. Then pentose unit decomposes to produce furfural. According to the thermo balance analysis, cellulose quantity is rapidly reduced at 250° - 350° and at this temperature range furfural production is rapidly increased. Also at this time, the break down of cellulose chemical structure is prominent. As the results of infra red absorption spectacle study Otani and others[4] confirmed the type cis double bond products due to the intra molecular dehydration of cellulose when heated above 250° and carbonyl radical products. Carbonyl radical in cellulose as thermal decomposition proceeds and high water content in the decomposition product indicates active dehydration reaction.

In the production lineage of cellulose to levoglucosan, a freeing of water molecule and carbonyl radical production do not take place. Also considering the results of furfural quantity comparison study, it is conceivable that in cellulose decomposition there is a line which does not go through levoglucosan.

Summary

1. As a result of the thermal decomposition of cellulose powder in atmosphere, a conspicuous reduction of cellulose quantity is illustrated at 250° - 350°. The change in chemical structure of cellulose and the increase in furfural production by thermal decomposition are also conspicuous at this temperature range.

2. Cellulose pyrolysis derivatives at 350^{o} are analyzed by paper chromatography and gas chromatography. As a result, formic acid, acetic acid, propion acid, iso-butyric acid, n-butyric acid, propionaldehyde, butylaldehyde, phenol and O(m) - cresol are confirmed. Also acetaldehyde and furfural are isolated and identified as 2,4-DNP.

The water content of decomposition product is 78.6%. Quantities of furfural and acids (formic acid and acetic acid) products are about 1.4% and 1.1% of cellulose respectively.

3. From the result of comparison analysis of furfural product quantity in cellulose and levoglucosan thermal decompositions, it is assumed that in cellulose thermal decomposition processes there exists a process which does not go through levoglucosan phase.

A summary of this research was presented at the Japan Agricultural Chemistry Society Convention of 1963.

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